5 **CATALYST STRUCTURE AND METHOD OF FISCHER-TROPSCH SYNTHESIS**

FIELD OF THE INVENTION

10   The present invention is a catalyst structure and method of making, and a method of Fischer-Tropsch synthesis.

BACKGROUND OF THE INVENTION

15   Fischer-Tropsch synthesis is carbon monoxide hydrogenation that is usually performed on a product stream from another reaction including but not limited to steam reforming (product stream H_2/CO ~3), partial oxidation (product stream H_2/CO ~2), autothermal reforming (product stream H_2/CO ~2.5), CO_2 reforming (H_2/CO ~1) coal gassification (product stream H_2/CO ~1) and

20 combinations thereof.

      Fundamentally, Fischer-Tropsch synthesis has fast surface reaction kinetics. However, the overall reaction rate is severely limited by heat and mass transfer with conventional catalysts or catalyst structures. The limited heat transfer together with the fast surface reaction kinetics may result in hot spots in

25 a catalyst bed. Hot spots favor methanation. In commercial processes, fixed bed reactors with small internal diameters or slurry type and fluidized type reactors with small catalyst particles (>50 μm) are used to mitigate the heat and mass transfer limitations. In addition, Fischer-Tropsch reactors are operated at lower conversions per pass to minimize temperature excursion in the catalyst

30 bed. Because of the necessary operational parameters to avoid methanation,

-1-

conventional reactors are not improved even with more active Fischer-Tropsch synthesis catalysts. Detailed operation is summarized in Table 1 and **FIG. 1**.

Table 1 - Comparison of Residence Times Effects in Fischer-Tropsch Experimentation

Ref[A]	Catalyst	Conditions	Residence time	Conversion	CH_4 selectivity
1	Co/ZSM-5	240°C, 20-atm, $H_2/CO=2$	3.6-sec	60 %	21 %
2	Co/MnO	220°C, 21-atm, $H_2/CO=2$	0.72-sec	13 %	15 %
3	Co-Ru/TiO$_2$	200°C, 20-atm, $H_2/CO=2$	3-sec	61 %	5 %
	Co/TiO$_2$	"	8-sec	49 %	7 %
4	Co/TiO$_2$	200°C, 20-atm, $H_2/CO=2.1$	2-sec	9.5 %	~9 %
	"	"	12-sec	72 %	~6 %
5	Ru/Al$_2$O$_3$	222°C, 21-atm, $H_2/CO=3$	4.5-sec	20 %	?
	"	"	7.2-sec	36 %	
	"	"	8.4-sec	45 %	
	"	"	9.6-sec	51 %	
	"	"	12-sec	68 %	
	"	"	14-sec	84 %	
6	Ru/Al$_2$O$_3$	250°C, 22-atm, $H_2/CO=2$	7.2-sec	38 %	5 %
7	Ru/ Al$_2$O$_3$	225°C, 21-atm, $H_2/CO=2$	12-sec	66 %	13 %
		222°C, 21-atm, $H_2/CO=3$	12-sec	77 %	34 %

For references that contained results for multiple experimental conditions, the run which best matched our conversion, selectivity and/or conditions was chosen for comparison of residence time.

(A) References
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5. Karn, F.S., J.F. Shultz and R.B. Anderson, *Ind. Eng. Chem. Prod. Res. Dev.* 4(4), 265 (1965).
6. King, F., E. Shutt and A.I. Thomson, *Platinum Metals Rev.* 29(44), 146 (1985).
7. Shultz, J.F., F.S. Karn and R.B. Anderson, *Rep. Invest. – U.S. Bur. Mines* 6974, 20 (1967).

Literature data (Table 1 and FIG. 1) were obtained at lower H_2/CO ratio (2:1) and longer residence time (3 sec or longer). Low H_2/CO (especially 2-2.5), long residence time, low temperature, and higher pressure favor Fischer-Tropsch synthesis. Selectivity to CH_4 can be significantly increased by increasing H_2/CO ratio from 2 to 3. Increasing residence time also has a dramatic favorable effect on the catalyst performance. Although reference 3 in Table 1 shows satisfactory

-2-

results, the experiment was conducted under the conditions where Fischer-Tropsch synthesis is favored (at least 3sec residence time, and $H_2/CO=2$). In addition, the experiment of reference 3 was done using a powdered catalyst on an experimental scale that would be impractical commercially because of the pressure drop penalty imposed by powdered catalyst. Operating at higher temperature will enhance the conversion, however at the much higher expense of selectivity to CH_4. It is also noteworthy that residence time in commercial Fischer-Tropsch units is at least 10 sec.

Hence, there is a need for a catalyst structure and method of Fischer-Tropsch synthesis that can achieve the same or higher conversion at shorter residence time, and/or at higher H_2/CO.

SUMMARY OF THE INVENTION

The present invention includes a catalyst structure and method of making the catalyst structure for Fischer-Tropsch synthesis that both rely upon the catalyst structure having a first porous structure with a first pore surface area and a first pore size of at least about 0.1 μm, preferably from about 10 μm to about 300 μm. A porous interfacial layer with a second pore surface area and a second pore size less than the first pore size is placed upon the first pore surface area. Finally, a Fischer-Tropsch catalyst selected from the group consisting of cobalt, ruthenium, iron, rhenium, osmium and combinations thereof is placed upon the second pore surface area.

Further improvement is achieved by using a microchannel reactor wherein the reaction chamber walls define a microchannel with the catalyst structure placed therein through which pass reactants. The walls may separate the reaction chamber from at least one cooling chamber.

The present invention also includes a method of Fischer-Tropsch synthesis having the steps of:

(a)   providing a catalyst structure having a first porous structure with a first pore surface area and a first pore size of at least about 0.1 μm;

a porous interfacial layer with a second pore surface area and a second pore size less than the first pore size, the porous interfacial layer placed upon the first pore surface area;

a Fischer-Tropsch catalyst selected from the group consisting of cobalt, ruthenium, iron rhenium, osmium and combinations thereof placed upon the second pore surface area; and

(b)   passing a feed stream having a mixture of hydrogen gas and carbon monoxide gas through the catalyst structure and heating the catalyst structure to at least 200 °C at an operating pressure, the feed stream having a residence time within the catalyst structure less than 5 seconds, thereby obtaining a product stream of at least 25% conversion of carbon monoxide, and at most 25% selectivity toward methane.

It is an object of the present invention to provide a catalyst structure for Fischer-Tropsch synthesis.

It is another object of the present invention to provide a method of Fischer-Tropsch synthesis having shorter residence time.

Advantages of the invention include (i) at residence time shorter than the prior art, higher conversions are achieved with no increase to methane selectivity; and (ii) as residence times increase, conversion increases and methane selectivity decreases (slightly). Surprisingly, the present invention represents an increase in conversion efficiency of at least a factor of 3 on the basis that equivalent conversion with conventional catalyst would require correspondingly greater residence time.

The subject matter of the present invention is particularly pointed out and distinctly claimed in the concluding portion of this specification. However, both the organization and method of operation, together with further advantages and objects thereof, may best be understood by reference to the following description

-4-

taken in connection with accompanying drawings wherein like reference characters refer to like elements.

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BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph of CO conversion versus residence time for prior art Fischer-Tropsch processes.

FIG. 2 is a cross section of a catalyst structure according to the present invention.

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DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

The present invention is a catalyst structure and method of making the
15   catalyst structure for Fischer-Tropsch synthesis which rely upon:

the catalyst is impregnated into a catalyst structure and calcined thereon. In a preferred embodiment, the catalyst structure is placed within a reaction chamber. The reaction chamber preferably has walls defining at least one microchannel through which pass reactants into the reaction chamber. The walls
20   preferably separate the reaction chamber from at least one cooling chamber. A microchannel has a characteristic dimension less than about 1 mm.

In order to mitigate the mass transfer limitation of the catalyst structure, the catalyst impregnation forms a porous interfacial layer that is less than 50 μm, preferably less than 20 μm. Therefore, the diffusion path length is at least a
25   factor of 5 shorter than for standard catalyst particles, and the catalyst structure is more active as indicated by the higher performance at shorter residence time. The thinner impregnated catalyst structure also enhances heat transfer, again due to the shorter heat transfer pathway, and leads to lower selectivity to CH_4.

In addition, because the catalyst structure is not required to be attrition
30   resistant as would be with the catalyst particles used in a fluidized bed reactor, greater porosity may be used, for example porosity greater than about 30%. Thus mass transfer is enhanced in the catalyst structure.

-5-

The catalyst structure may be any geometric configuration including but not limited to foam, felt, wad and combinations thereof. Foam is a structure with continuous walls defining pores throughout the structure. Felt is a structure of fibers with interstitial spaces therebetween. Wad is a structure of tangled strands, like steel wool.

When the first porous structure is metal, its surface is passivated and coated with a ceramic layer using a chemical vapor deposition (CVD) method as described in U.S. patent application 09/123,781 (E-1666A) hereby incorporated by reference. The catalyst structure of the present invention is depicted in **FIG. 1** having a catalyst support **100** of a first porous structure, a buffer layer **102** (optional), an interfacial layer **104**, and, a catalyst or catalyst layer **106**. Any layer may be continuous or discontinuous as in the form of spots or dots, or in the form of a layer with gaps or holes. Continuous layer of buffer layer **102** is preferred.

The interfacial layer **104** is a metal oxide. The metal oxide includes but is not limited to γ-Al$_2$O$_3$, SiO$_2$, ZrO$_2$, TiO$_2$, magnesium oxide, vanadium oxide, chromium oxide, manganese oxide, iron oxide, nickel oxide, cobalt oxide, copper oxide, zinc oxide, molybdenum oxide, tin oxide, calcium oxide, aluminum oxide, lanthanum series oxide(s), zeolite(s) and combinations thereof. Typically the porous support **100** has a thermal coefficient of expansion different from that of the interfacial layer **104**. Accordingly, for high temperature catalysis (T > 150 °C) a buffer layer **102** may be needed to transition between the two coefficients of thermal expansion. Another advantage of the buffer layer **102** is avoiding side reactions such as coking or cracking caused by a bare metal foam surface. For chemical reactions which do not require large surface area supports such as catalytic combustion, the buffer layer **102** stabilizes the catalyst metal due to strong metal to metal-oxide interaction. In chemical reactions which require large surface area supports, the buffer layer **102** provides stronger bonding to the high surface area interfacial layer **104**.

-6-

The buffer layer **102** is a metal oxide that is Al_2O_3, TiO_2 , SiO_2, and ZrO_2 and combinations thereof. More specifically, the Al_2O_3 is α-Al_2O_3, γ-Al_2O_3 and combinations thereof. The structure of the α-Al_2O_3 is preferred since it is most resistant to oxygen diffusion. Therefore, it is expected that resistance against

5   high temperature oxidation can be improved with alumina coated on the porous support **100**. When the porous support **100** is metal foam, for example a stainless steel foam, a preferred embodiment has a buffer layer **102** formed of two sub-layers (not shown). The first sublayer (in contact with the porous support **100**) is TiO_2 for good adhesion and bonding of the ceramic layers to the

10   porous support **100**. The second sublayer is α-Al_2O_3 which is used for passivating the metal foam and is placed upon the TiO_2.

Deposition of the buffer layer **102** may be by vapor deposition including but not limited to chemical vapor deposition, physical vapor deposition or combinations thereof. Because the vapor deposition is conducted at high

15   temperatures, polycrystalline phases are formed providing good adhesion of the metal oxide to the metal foam surface. Alternatively, the buffer layer **102** may be obtained by solution coating. For example, the solution coating has the steps of metal surface functionalization via hydroxide formation, followed by surface hydrolysis of alkoxides to obtain the polycrystalline phases. This solution coating

20   may be preferred as a lower cost method of depositing the buffer layer **102**. Polycrystalline metal oxides resist flaking of layers after several thermal cycles.

Because metal foam has web surfaces that are nonporous and smooth, deposition of the interfacial layer may be impeded. One way to mitigate this problem is to rough the metal foam surface via chemical etching. The adhesion

25   of high surface area gamma-alumina supported metal catalysts to metal foam is significantly improved when metal foam is roughed via chemical etching using mineral acid solutions, for example HCl. Roughed web surface also shows improved resistance to the spalling of catalyst layer under thermal cyclings. The open cells of a metal foam may range from about 20 ppi (pores per inch) to about

30   1000 ppi and is preferably about 80 ppi.

-7-

Catalyst metals for Fischer-Tropsch synthesis include but are not limited to iron (Fe), cobalt (Co), ruthenium (Ru), rhenium (Re), osmium (Os) and combinations thereof.

The use of the catalyst impregnated metal foam permits residence time less than about 5 seconds, preferably from about 1 sec to about 2 sec. The reactor will scale up with modular reactors, which will provide at least a factor of 3 enhancement of equivalent activity.

According to the method of the present invention, residence time less than 5 seconds is achieved by: (a) providing a catalyst structure of a metal foam having a catalyst thereon; and (b) passing a feed stream having a mixture of hydrogen gas with carbon monoxide gas through the catalyst structure and heating the catalyst structure to at least 200 °C, thereby obtaining a product stream of at least 25% conversion of carbon monoxide, and at most 25% selectivity toward methane. In a preferred method, the catalyst structure includes a buffer layer and an interfacial layer with the catalyst impregnated onto the interfacial layer. The ratio of hydrogen to carbon monoxide ranges from about 1:1 to about 6:1, preferably from about 2:1 to about 3.5:1.

Residence time less than 5 seconds may be accomplished with standard equipment but at the expense of significant energy to raise the space velocity of the reactants to overcome the pressure drop and poorer heat transfer leading to higher methane formation. Heat transfer from the reaction chamber is preferably enhanced by addition of microchannels on at least one reaction chamber wall on the side of the reaction chamber wall opposite the catalyst structure.

It was unexpectedly discovered that by using the catalyst structure of the present invention, reducing the pressure of the Fischer-Tropsch reaction resulted in increased yield, less selectivity toward methane.

Example 1

A reactor was constructed with a reaction chamber with an inlet and an outlet. Internal reactor chamber dimensions were length 35.6 mm (1.4 in), height 1.5 mm (0.060 in) and width 8mm (0.315 in).

Catalyst impregnated metal foam was made starting with a metal foam of stainless steel having a porosity of 90% as obtained from Astro Met, Cincinnati, Ohio. Foam metal surface was passivated and coated with a ceramic layer as described above.

15wt%Co1wt%Ru/γ-Al$_2$O$_3$ was synthesized in house using incipient wetness method. The powdered catalyst was ball-milled overnight and slurry dip-coated on foam metal until the desired loading was achieved. The coated catalyst was dried overnight and calcined at 350°C for four hours.

In this experiment, two catalyst materials were used with exactly the same composition but in different physical form. Both catalyst materials had 15wt%Co1wt%Ru/γ-Al$_2$O$_3$. One was in powder form tested in a micro fixed-bed reactor according to literature specification for minimizing the heat and mass transfer resistance. The other was a catalyst impregnated metal foam tested in a single channel testing unit.

Results are shown in Table E1-1. Even though both catalysts were tested under the identical conditions, powdered catalyst shows significantly higher conversion (99.6%) and higher selectivity to undesired product CH$_4$ (36%), apparently due to un-measured temperature excursions within catalyst bed.

-9-

TABLE E1-1 Fischer-Tropsch Catalyst Performance

Catalyst	Conditions	Residence time	Conversion	CH_4 selectivity
Co-Ru/Al$_2$O$_3$/ foam	231°C, 23-atm, H$_2$/CO=3	1-sec	17 %	9.6 %
"	247°C, 23-atm, H$_2$/CO=3	1-sec	29 %	15 %
"	264°C, 23-atm, H$_2$/CO=3	1-sec	50 %	22 %
"	264°C, 23-atm, H$_2$/CO=3	1-sec	49 %	22 %
"	275°C, 23-atm, H$_2$/CO=3	1-sec	69 %	24 %
"	275°C, 23-atm, H$_2$/CO=3	2-sec	84 %	9.0 %
"	245 °C, 23 atm, H$_2$/CO =3	1-sec	33%	12%
Co-Ru/Al$_2$O$_3$/ powder	245 °C, 23 atm, H$_2$/CO =3	1-sec	99.6%	36%

Example 2

An experiment was conducted to demonstrate operation at various pressures. The equipment was the same as in Example 1.

According to the literature, variation in pressure should only affect true residence time in Fischer-Tropsch synthesis. In other words, conventional wisdom in Fischer-Tropsch reactions is that reaction rate is proportional to pressure under identical gas hourly space velocity (GHSV).

However, as shown in Table E2-1, with the catalyst structure of the present invention, catalyst activity was unexpectedly enhanced as the pressure was decreased under the same temperature and pressure corrected residence time. This surprising result is attributed to the enhanced mass and heat transfer possible with the catalyst structure of the present invention.

Table E2-1 - Engineered catalyst performance for Fischer-Tropsch synthesis at 265°C under a temperature and pressure corrected residence time of 12.5 seconds.

Pressure, atm	Conversion, %	Selectivity to CH_4, %
5	63	18
6	41	22
10	34	19
23	24	26

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10 Example 3

Use of Co or Ru alone as a catalyst on the metal foam was also tested under the conditions of Example 1 and performance was confirmed worse than that of bimetallic catalyst such as Co-Ru.

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CLOSURE

20   While a preferred embodiment of the present invention has been shown and described, it will be apparent to those skilled in the art that many changes and modifications may be made without departing from the invention in its broader aspects. The appended claims are therefore intended to cover all such changes and modifications as fall within the true spirit and scope of the invention.